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14. ABSTRACT

A specific capacitance of about 300 F/g was achieved by KOH activated PAN/CNT films as compared to less than 120 F/g achieved for CO2 activated samples. The PAN/CNT (80/20) film impregnated with 6M KOH and activated at 800 °C resulted in maximum specific capacitance. Samples activated at all process conditions resulted in narrow pore size distribution of 1-5 nm. The specific capacitance measured from this study correlated to micropore surface areas. The energy density increased from ~ 2 Wh/Kg in 6M KOH to ~ 22 Wh/kg in BMIMBF4/AC by increasing the operating voltage from 0.8 V to 3.0 V respectively. The energy density (~ 22Wh/kg) achieved from this study is in the range obtained for batteries. Capacitance of KOH activated PAN/CNT (80/20) films even after 10,000 charge/discharge cycles, was substantially higher that that for the KOH activated buckypapers. Electrospun PAN, PAN/SAN, and PAN/SAN/CNT fiber mats as well as bulk composite films were also stabilized, carbonized, and processed into electrochemical capacitor electrodes. Results of these studies are also reported.

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Executive Summary:

Poly(acrylonitrile) (PAN) based nanofibers were electrospun with controlled diameter. A sacrificial polymer, poly(styrene-co-acrylonitrile) (SAN) has been used to control porosity. Carbon nanotubes (CNT) have been used to increase electrode conductivity and hence power density. The diameter of electrospun PAN fibers was monitored as a function of polymer molecular weight, solution concentration, solution flow rate, distance between the spinneret and the target, and the applied voltage. Bead free PAN fibers of 60 nm diameter have been electrospun. Various electrospun fibers have been characterized by wide angle X-ray diffraction and by Raman spectroscopy. Electrospinning process has been observed by high speed photography.

Electrospun PAN, PAN/SAN, and PAN/SAN/CNT fiber mats were stabilized, carbonized, and processed into electrochemical capacitor electrodes. The performance of the electrochemical capacitors was tested by the constant current charge/discharge and cyclic voltammetry in 6 molar potassium hydroxide aqueous solution. The surface area and pore size distribution of the electrodes were measured using N_2 adsorption and desorption. The effect of surface area and pore size distribution on the capacitance performance has been studied. The capacitance performance of various carbonized electrospun fiber mats have been compared to those of the PAN/SAN/CNT film, carbon nanotube bucky paper, and activated carbon pellet. The capacitance of PAN/SAN/CNT fiber mat over 200 F/g (at a current density of 1 A/g) and the power density approaching 1 kW/kg have been observed. Addition of 1 wt% carbon nanotubes in PAN/SAN, improves the power density by a factor of four. For comparison, the capacitance of single wall carbon nanotube bucky paper at a current density of 1 A/g is about 50 F/g.

Carbonized PAN/SAN/SWNT ternary composite films exhibit double layer capacity of over 200 $\mu F/cm^2$. By comparison, the double layer capacity of classical meso-porous carbons is in the range of 10-50 $\mu F/cm^2$. The capacitance of functionalized SWNTs is up to 2 times that of the control bucky paper made from unfunctionalized SWNTs.

In order to electrospin SWNT/PMMA/nitromethane solution into composite nanofibers, first PMMA was electrospun over a wide concentration range. With increasing solution concentration, morphology of the electrospun polymer changed from particles to fibers. At relatively low solution concentrations, micro- and nano-structured polymer particles (including cups), and at higher solution concentrations, porous and solid nanofibers are observed. SWNT/PMMA/nitromethane solution was electrospun into polymer shell-SWNT core nanofibers. Solvent characteristics play an important role on particle or fiber mat morphology during electrospinning. The qualitative relationship between solvent properties (evaporation rate, dielectric constant, surface tension, and viscosity) and particle morphologies is discussed. By tailoring solution properties and electrospinning conditions, one can produce particles or fibers with controlled morphology for specific applications.

Structure and electrochemical properties of polyacrylonitrile (PAN)/carbon nanotube (CNT) composite film and fiber based electrodes developed for electrochemical capacitors have been investigated. Films are prepared by solution casting and fibers are spun by solution spinning, and gel spinning methods. The PAN/CNT film and fiber precursors are stabilized in air, carbonized in inert atmosphere (argon), and activated by physical (CO_2) and chemical (KOH) methods.

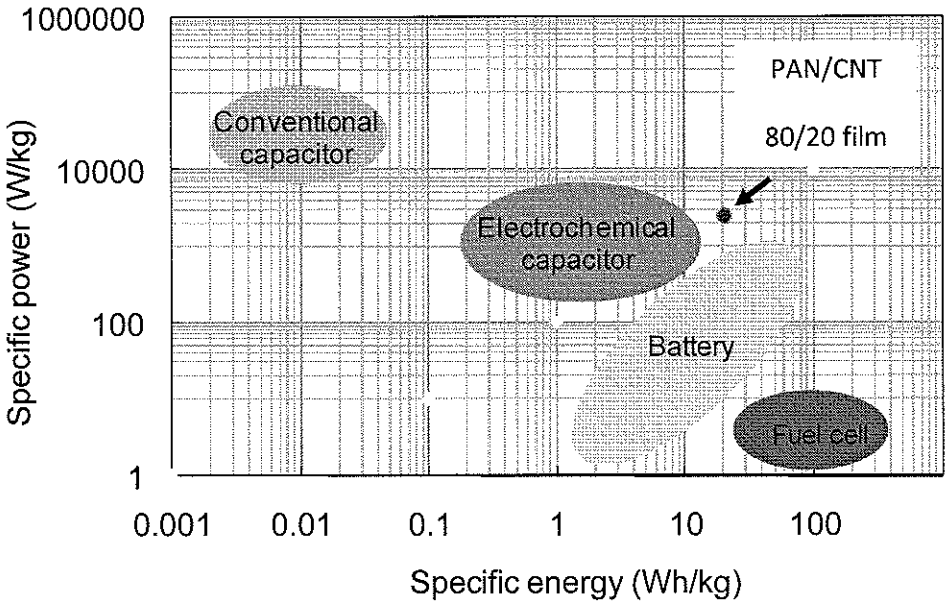
For CO_2 activated PAN/CNT films, sample with 80/20 PAN/CNT ratio activated at 900 °C resulted in highest surface area and specific capacitance. Specific capacitance increased with activation time and temperature and has direct correlation with micropore surface area. Wide pore size distributions of 1 – 250 nm were obtained for samples activated at all process conditions. Surface areas less than 700 m^2/g and pore volume less than 0.2 cm^3/g were obtained for physically activated PAN/CNT films.

The electrochemical properties and surface areas from physical and chemical activation processes were compared for solution spun PAN/CNT fibers. The surface areas as determined by nitrogen gas adsorption was an order of magnitude higher for KOH activated fibers as compared to the CO_2 activated fibers. Under the comparable KOH activation conditions, PAN and PAN/SWNT fibers had comparable surface areas (BET surface area about 2200 m^2/g) with pore size predominantly in the range of 1 to 5 nm, while surface area of PAN/MWNT samples was significantly lower (BET surface area 970 m^2/g). The highest capacitance and energy density was obtained for PAN/SWNT samples, suggesting SWNT advantage in charge storage. The capacitance behavior of these electrodes has also been tested in ionic liquids, and the energy density in ionic liquid is higher than the value obtained using KOH electrolyte.

The gel spun fibers with higher polymer molecular orientation, higher CNT orientation and exfoliation were activated using chemical activation process. The specific capacitance of KOH activated gel-spun PAN fiber samples was as high as high as 240 F/g in 6M KOH electrolyte. Under the comparable KOH activation conditions, spin drawn as well as drawn gel spun PAN and PAN/SWNT fibers resulted in higher BET surface areas with pore size predominantly in the range of 1 to 5 nm, while surface area of the comparably processed PAN/MWNT samples was significantly lower. Energy densities increased from ~2 Wh/Kg in 6M KOH to a maximum of ~ 22 Wh/Kg in $BMIMBF_4$/AC at 0.1mA constant current for as spun PAN fibers by increasing the operating voltage from 0.8 V to 3.0 V respectively.

The SWNT and MWNT buckypaper electrodes on chemical activation showed increased surface area, pore volume, specific capacitance, and energy density. The activation process does not alter the d-spacing of CNTs as verified by WAXD results and does not introduce any functional groups onto the CNT surface as verified by FTIR. The increase in specific capacitance achieved for activated SWNT and MWNT buckypaper is sustained for 10000 cycles making it an attractive candidate for energy storage application.

The chemical activation process variables like activation temperature, molarity of impregnating agent, and composition of PAN/CNT films were varied to determine process condition to achieve highest electrochemical properties and surface areas. A specific capacitance of ~ 300 F/g was achieved by KOH activated PAN/CNT films as compared to less than 120 F/g achieved for CO_2 activated samples. The PAN/CNT (80/20) film impregnated with 6M KOH and activated at 800 °C resulted in maximum specific capacitance. Samples activated at all process conditions resulted in narrow pore size distribution of 1-5 nm. The specific capacitance measured from this study correlated to micropore surface areas. The energy density increased from ~ 2 Wh/Kg in 6M KOH to ~ 22 Wh/kg in $BMIMBF_4$/AC by increasing the operating voltage from 0.8 V to 3.0 V respectively. The energy density (~ 22Wh/kg) achieved from this study is in the range obtained for batteries as given in the following Figure. Capacitance of KOH activated PAN/CNT (80/20) films even after 10,000 charge/discharge cycles, was substantially higher that that for the KOH activated buckypapers.



A comparison of maximum energy density and power density achieved in this thesis to typical values for energy storage devices.

A specific capacitance of 250 - 300 F/g and surface areas ~ 2500 m^2/g were consistently achieved by chemical activation of films, solution spun fibers and gel spun fibers. The chemical activation process is therefore quite promising for developing next generation energy storage devices.

Key Personnel: Satish Kumar, Chongfu Zhou, Tong Wang, Jing Liu, Sudhakar Jagannathan, Shanju Zhang, Han Gi Chae, Rahul Jain, Asif Rasheed, Marilyn Minus

Theses:

1. C. Zhou, Ph.D. Thesis, "Carbon Nanotube Based Electrochemical Supercapacitors", December 2006, Georgia Institute of Technology, Atlanta GA.
2. T. Wang, Ph.D. Thesis, "Electrospun Carbon Nanofibers for Electrochemical Capacitor Electrodes", May 2007, Georgia Institute of Technology, Atlanta GA.
3. J. Liu, Ph.D. Thesis, "Carbon Nanotube/Polymer Composites and Novel Micro- and Nano-structured Electrospun Polymer Materials", May 2007, Georgia Institute of Technology, Atlanta GA.
4. S. Jagannathan, Ph.D. Thesis, "Process, Structure and Electrochemical Properties of Carbon Nanotube Containing Films and Fibers", August 2009, Georgia Institute of Technology, Atlanta GA

These theses are readily available in electronic form from Georgia Tech library at the following website: http://www.library.gatech.edu/

Publications:

1. C. Zhou, T. Liu, T. Wang, S. Kumar, "SWNT/PAN/SAN ternary composite: Pore Size Control and Electrochemical Supercapacitor Behavior", *Polymer,* **47**, 5831-5837 (2006).
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7. S. Jagannathan, S. Kumar, "Pore size control and electrochemical capacitor behavior of chemically activated polyacrylonitrile - carbon nanotube films", submitted for publication.